

Solid-State Inorganic Nanofiber Network-Polymer Composite Electrolytes for Lithium Batteries

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Merit Review**

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Project ID: bat321

Timeline

- **Project Start Date: Oct. 1, 2016**
- **Project End Date: Sept. 30, 2019**
- **Percent complete: 55% (till 03/31 2018)**

Budget

- **Total project funding**
 - **DOE share:\$1,244,012**
 - **Contractor share: \$156,181**
- **Funding received in FY 2017: \$479,720**
- **Funding for FY 2018: \$463,711**

Barriers

- **Poor conductivity of current composite electrolytes (10^{-6} S/cm to 10^{-4} S/cm)**
- **Low mechanical strength of composite electrolytes**
- **Low stability during operation**

Partners

- **Interactions/collaborations: North Carolina State University**
- **Project lead: West Virginia University**

Relevance

Overall objectives

Develop the solid-state electrolytes by integrating a highly-conductive inorganic nanofibrous network in a conductive polymer matrix for both lithium metal and lithium-sulfur batteries.

Objectives of this period (04/01/2017– 03/31/2018)

- Synthesize the inorganic nanofiber-polymer composite electrolytes;
- Characterize the microstructure of composite electrolytes, and study the nanofiber-polymer interface;
- Measure the temperature-dependent ionic conductivity of composite electrolytes and electrochemical stability window, mechanical property.

Impact

The DOE funding will allow the research team to develop solid-state inorganic nanofiber-polymer composite electrolytes that will not only provide higher ionic conductivity, improved mechanical strength and better stability than the PEO-based polymer electrolyte, but also exhibit better mechanical integrity, easier incorporation and better compatibility with the lithium metal anode than the planar ceramic membrane counterparts. The proposed inorganic nanofiber-polymer composite electrolytes will enable the practical use of high energy-density, high power-density lithium metal batteries and lithium-sulfur batteries.

Milestones

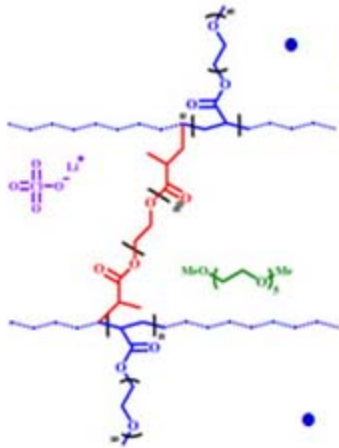
Milestones in Year 1:

Milestone	Type	Description
Synthesize inorganic nanofibers	Technical	Demonstrate inorganic nanofiber samples
Inorganic nanofiber testing	Technical	Test the conductivity of inorganic nanofibers, achieving ion conductivity of >1.0 mS/cm
Synthesize polymers	Technical	Demonstrate polymer samples
Polymer testing	Technical	Test the conductivity of polymers achieving >0.2 mS/cm
Develop the ion-conducting polymers and inorganic nanofibers	Go/No Go	Approach identified to optimize ion-conducting polymers and inorganic nanofibers.

Milestones in Year 2:

Milestone	Type	Description
Synthesize composite electrolytes	Technical	Demonstrate nanofiber polymer composite samples
Performance of composite electrolytes	Technical	Measure electrochemical performance of composite electrolytes achieving >0.8 mS/cm; decomposition voltage >4.5 vs. Li^+/Li
Properties of composite electrolytes	Technical	Measure the mechanical properties such as the Young's modulus, the shear modulus and tensile and shear strengths
Develop inorganic nanofiber-polymer composite electrolytes	Go/No Go	Approach identified to optimize development of inorganic nanofiber-polymer composite electrolytes

Approach



• Design and engineer the polymer matrix

Develop the block copolymers or cross-linked polymers that have higher ionic conductivity than traditional polyethylene oxide (PEO) polymers.

Approach identified to optimize ion-conducting polymers and inorganic nanofibers.



• Design and engineer the inorganic nanofibers

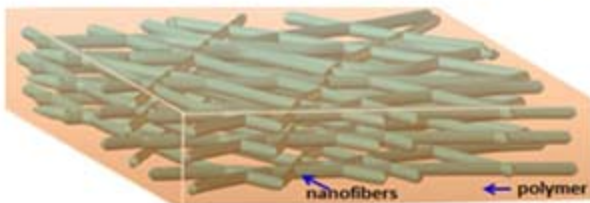
- Provide continuous Li^+ transport channels via nanofiber network
- Inhibit crystallization of amorphous polymer electrolyte
- Facilitate lithium salt dissociation and ion transport through the polymer electrolyte

Approach identified to optimize development composite electrolytes.



• Enhance the synergistic effect of integrated inorganic fiber-polymer composites

- In-situ polymerization
- Design linker to couple the nanofibers to the polymer matrix
- Design deliberately to suppress the formation of lithium dendrites
- Measure the mechanical and electrochemical properties of composites
- Optimize the nanofiber-polymer composites



Approach

Innovation

Polymer matrix:

- Compared with the complicate synthesis procedures reported before, such as ring opening polymerization, our cross-linked acrylate-based PEO polymers are fabricated through easy **UV cross-linking** process.
- Compared with the crystalline PEO structure, ours has **fully amorphous PEO structure**.
- Compared with previous double cross-linkers with high T_g (-20 °C), our polymer is plasticized with PEG, showing **low glass transition temperature** T_g (-56.5 °C).
- Compared with the low ionic conductivity of the previous PEO based polymers (10^{-9} - 10^{-6} S/cm), ours has **higher ionic conductivity**, for example the salt-added cross-linked polymer can reach an ionic conductivity of 2.4×10^{-4} S/cm.

Inorganic nanofibers:

- **Hydrogen-treatment** is performed to **create oxygen vacancies** in Li-conducting metal oxides, showing improved ionic conductivity
- Li-conducting metal oxides are **doped with anions (nitrogen)** while cation doping is reported in previous studies. Nitrogen doping can create the stable oxygen vacancy in the metal oxides.

Ceramic-polymer composite electrolyte:

- Composite electrolytes are prepared with **in-situ polymerization** on the ceramic nanofiber network.
- **Grating agent** is introduced at the ceramic/polymer interface in the composite.
- The ceramic nanofibers are **surface-modified** with a high ionic conductivity buffer layer, which is located at the ceramic/polymer interface in the composite.

Full-cell batteries:

- All-solid-state Li-ion batteries are developed, which greatly improves the **safety** during operation.
- Use of solid-state electrolyte **suppresses the dendrite formation**.
- All-solid-state Li-ion batteries show **excellent cycle-stability**, including high capacity retention and high columbic efficiency

Technical Accomplishments and Progress

Previous Accomplishments in Year 1 (10/01/2017 ~ 03/31/2018):

- ☐ synthesized three precursors and monomers for block co-polymers
- ☐ prepared a block co-polymer
- ☐ synthesized three different types of inorganic nanofibers.

Technical Accomplishments and Progress

Work done in Year 2 (04/01/2017 ~ 03/31/2018):

Polymer matrix:

- Block copolymer
- Cross-linked block copolymer
- Salt-added Cross-linked polymer

Inorganic nanofibers:

- Aluminum-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLATO) nanofibers
- Nitrogen-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (N-LLTO) nanofibers

Ceramic-polymer composite electrolyte:

- LLTO incorporated into the cross-linked polymer composite
- Silane linker at the LLAZO/polymer interface in the composite
- Lithium phosphate at the LLATO/polymer interface in the composite

Coin-cell battery:

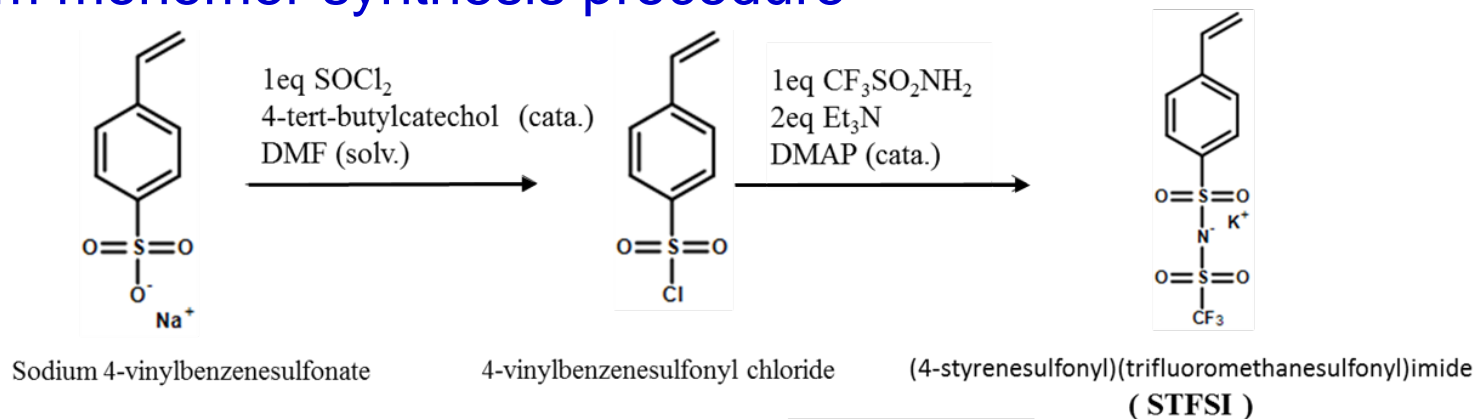
- Cycling performance, Coulombic efficiency and charge/discharge curves of the $\text{Li} | \text{CLP-P4-LLTO} | \text{LFP}$ battery

Current Progress in

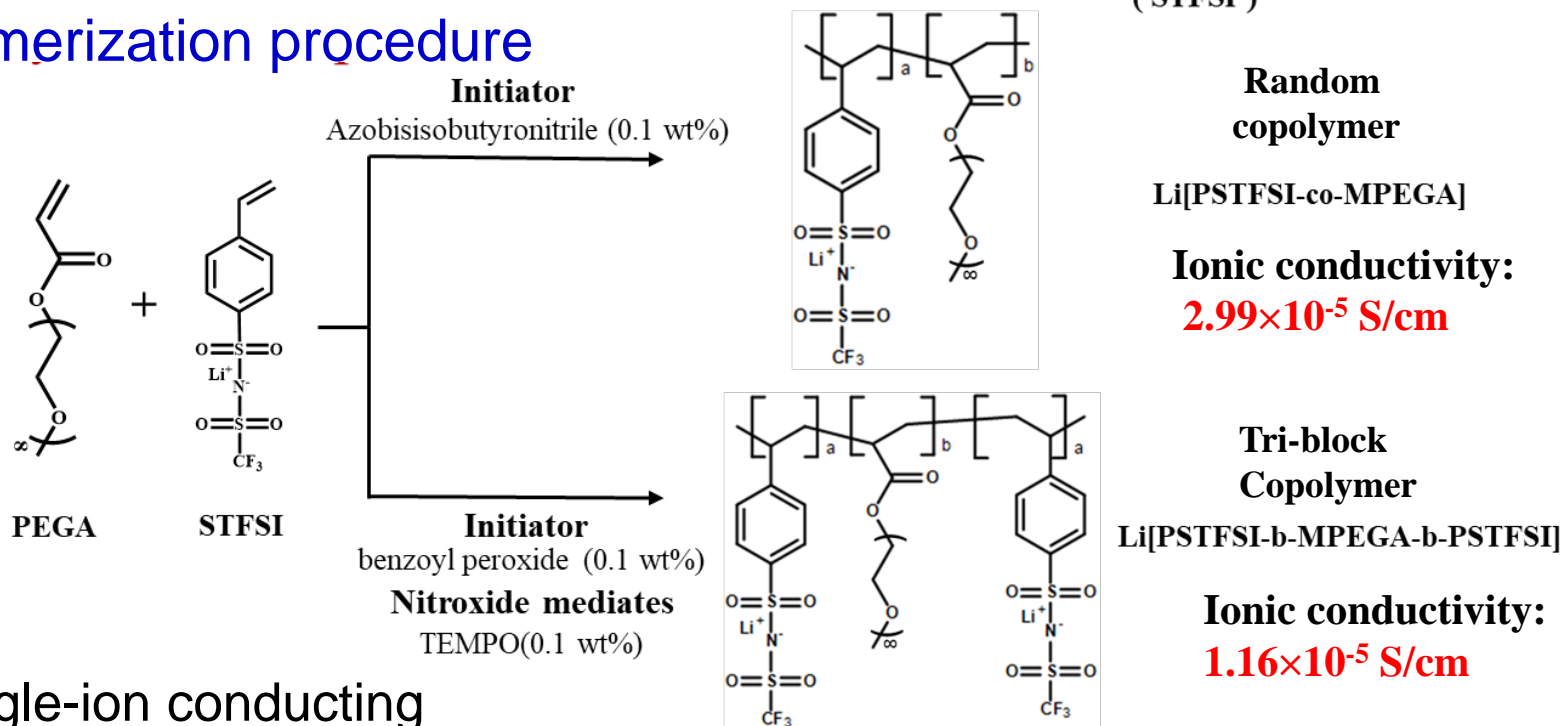
POLYMER MATRIX

Polymer matrix development 1: *Block copolymer*

Lithium monomer synthesis procedure



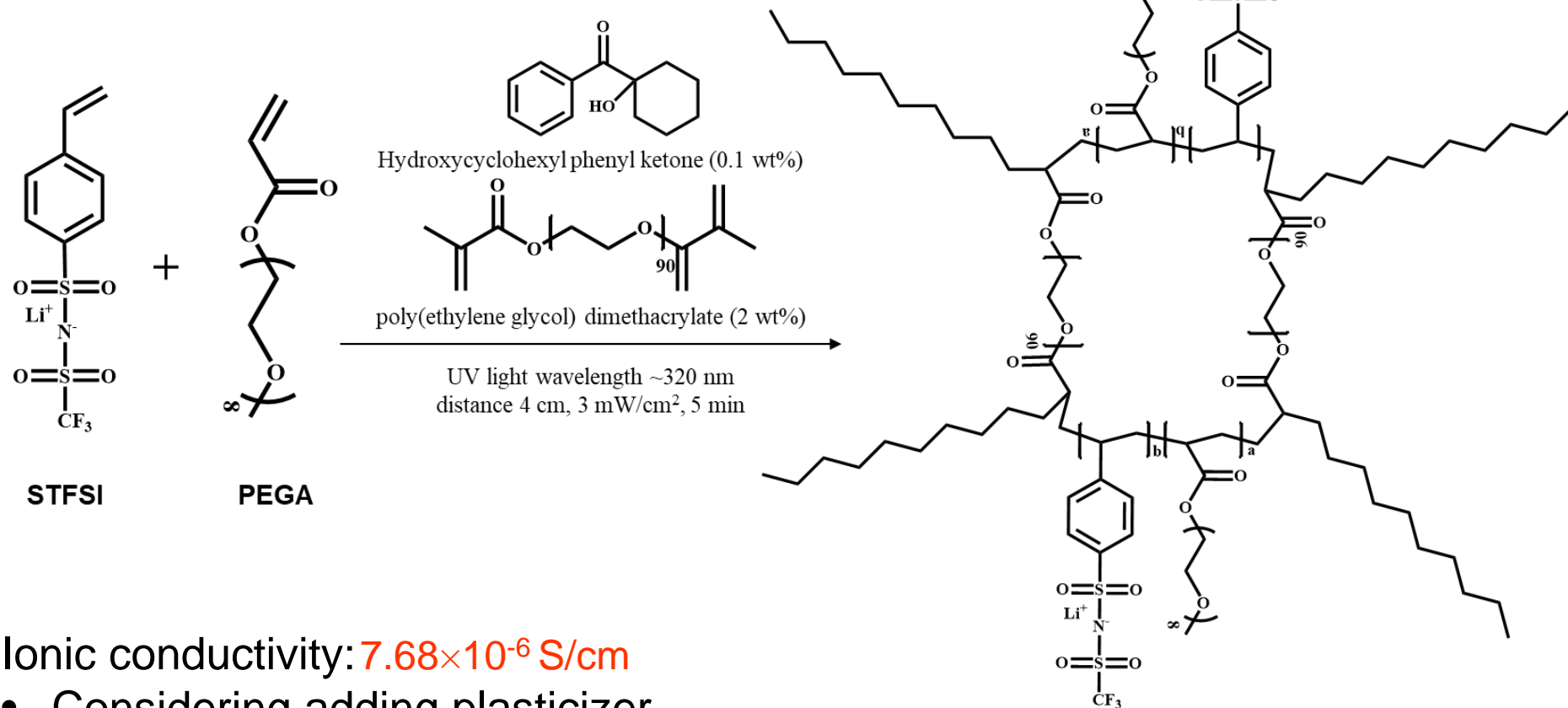
Polymerization procedure



- Single-ion conducting
 - Supper-delocalized polyanion PSTFSI

Polymer matrix development 2: *Cross-linked block copolymer*

Synthesis procedure:

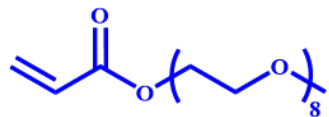


Ionic conductivity: $7.68 \times 10^{-6} \text{ S/cm}$

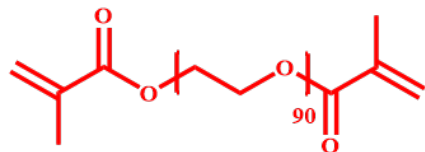
- Considering adding plasticizer
- Single-ion conducting channel
- High mechanical strength
 - Lithium blocks have higher rigidity

Polymer matrix development 3: Salt-added Cross-linked polymer

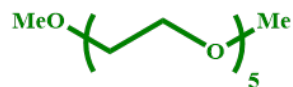
Synthesis procedure:



Poly(ethylene glycol) acrylate
Monomer (PEGA)

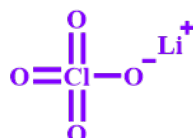


Poly(ethylene glycol) dimethacrylate (2 wt%)
Cross Linker (PEGDMA)



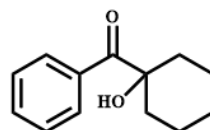
Dimethyl
Poly(ethylene glycol)

Plasticizer (PEG)



LiClO₄

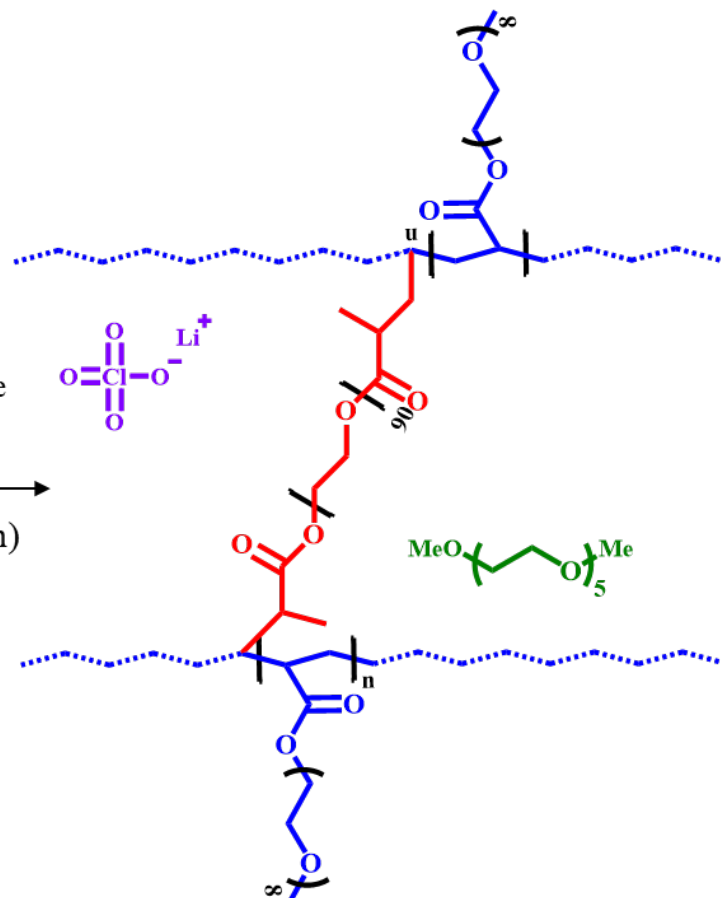
[EO]/[Li⁺] = 20 : 1



Hydroxycyclohexyl phenyl ketone
(0.1 wt%)

Photo Initiators (HCPK)

UV light (wavelength ~320 nm)
3 mW/cm², 5 min

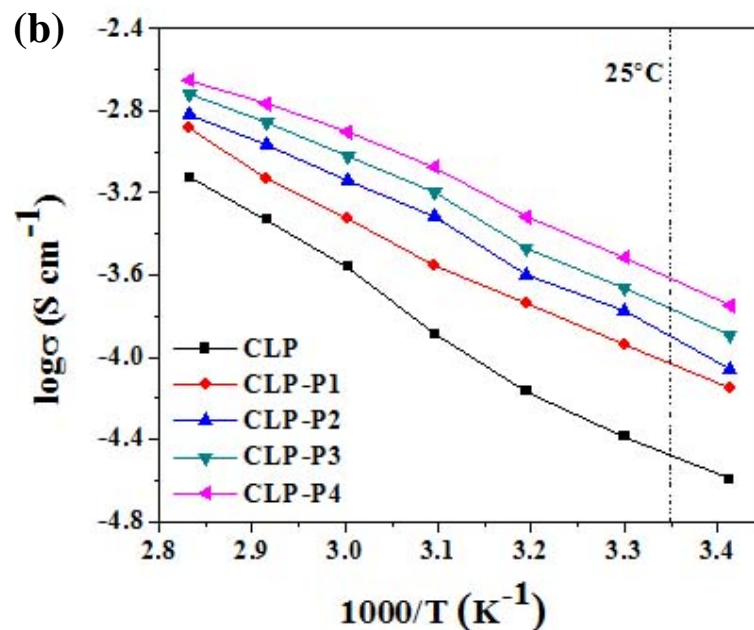
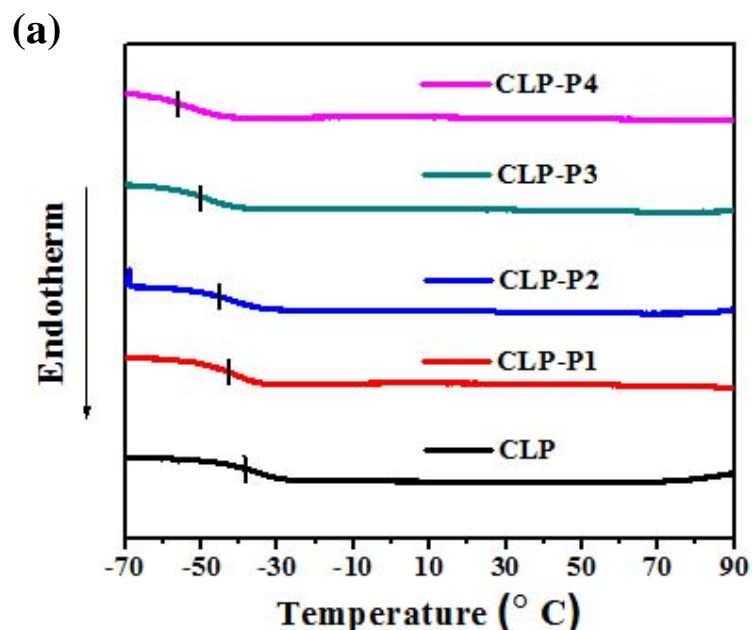


**Cross-linked poly(ethylene oxide) polymer matrix
Plasticized (CLP-P)**

- High ionic conductivity polymer matrix
 - Naturally amorphous structure
 - Small molecular weight chains move freely (decrease in T_g)

Polymer matrix development 3: Salt-added Cross-linked polymer

Thermal properties and ionic conductivity:



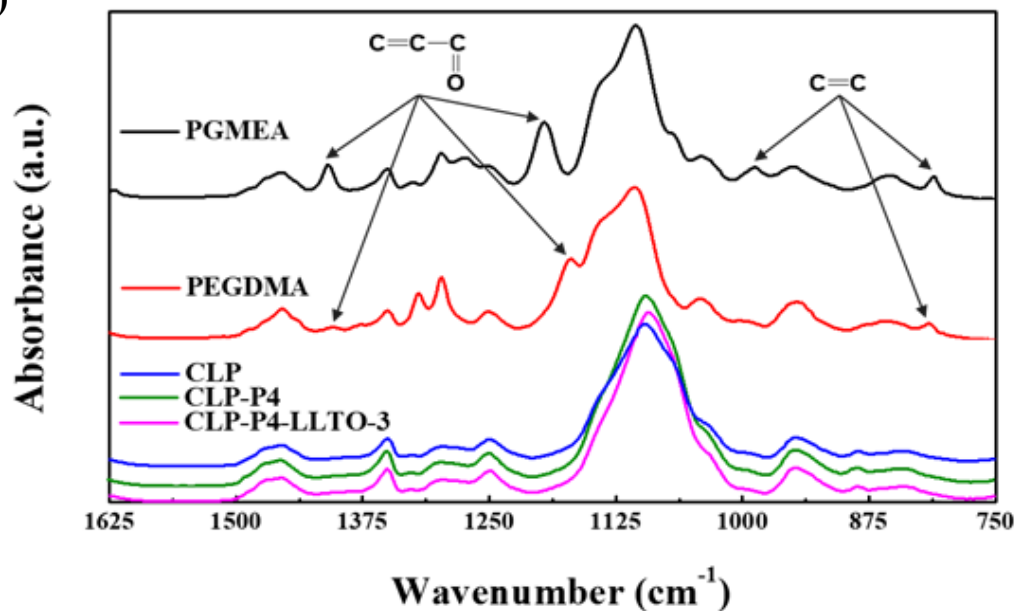
- No melting transition
- Low glass transition temperature (-56.5 $^{\circ}\text{C}$)
- Adding PEG increases ionic conductivity
 - Decrease in T_g
 - Decrease in E_a

	PEG amount (wt %)	T_g ($^{\circ}\text{C}$)	Ionic conductivity at 25 $^{\circ}\text{C}$ (S/cm)	Activation Energy (E_a) (eV)
CLP	0	-39.2	3.38×10^{-5}	0.53
CLP-P1	10	-42.1	9.36×10^{-5}	0.43
CLP-P2	20	-45.3	1.28×10^{-4}	0.43
CLP-P3	30	-50.3	1.75×10^{-4}	0.42
CLP-P4	40	-56.5	2.40×10^{-4}	0.40

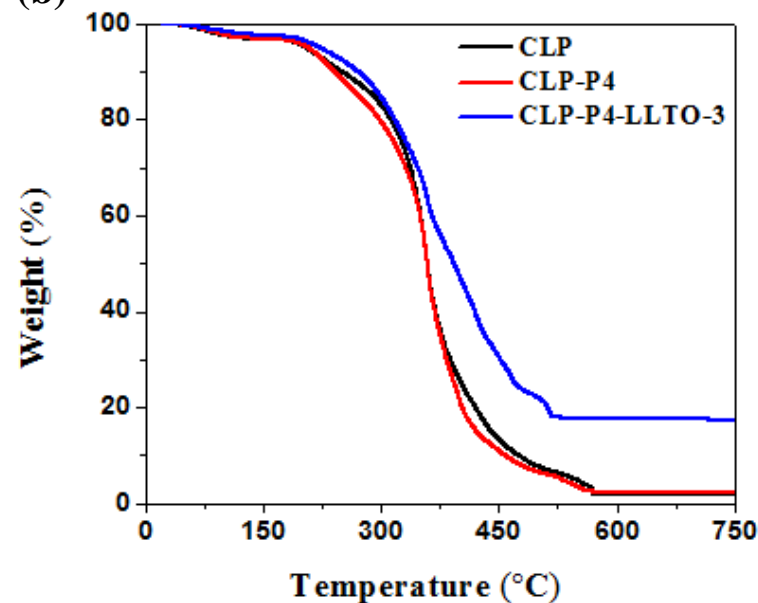
Polymer matrix development 3: Salt-added Cross-linked polymer

Chemical Structure:

(a)



(b)



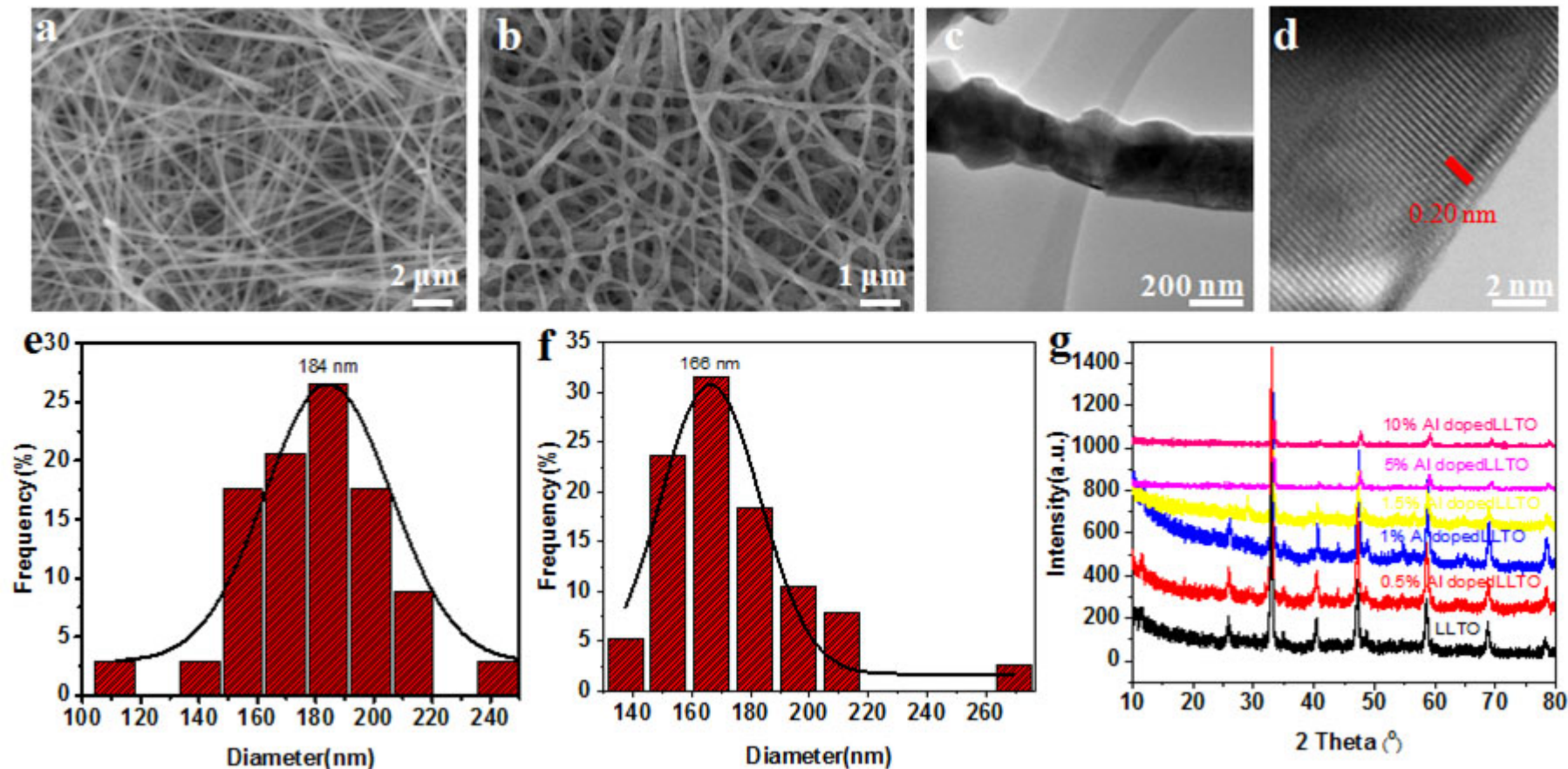
- Peaks of vinyl group ($\text{C}=\text{C}$) and acrylate group ($\text{C}=\text{C}-\text{C}=\text{O}$) disappeared after polymerization
 $\nu = 988, 812, 1190, 1410 \text{ cm}^{-1}$ (PGMEA)
 $\nu = 817, 1175 \text{ cm}^{-1}$ (PEGDMA)
- Monomers are totally reacted and cross linked even with addition of plasticizer and nanofibers
- Good thermal stability
 - Thermal degradation temperature 400 $^{\circ}\text{C}$

Current Progress in

INORGANIC NANOFIBERS

Inorganic Nanofibers: *Al-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLATO)*

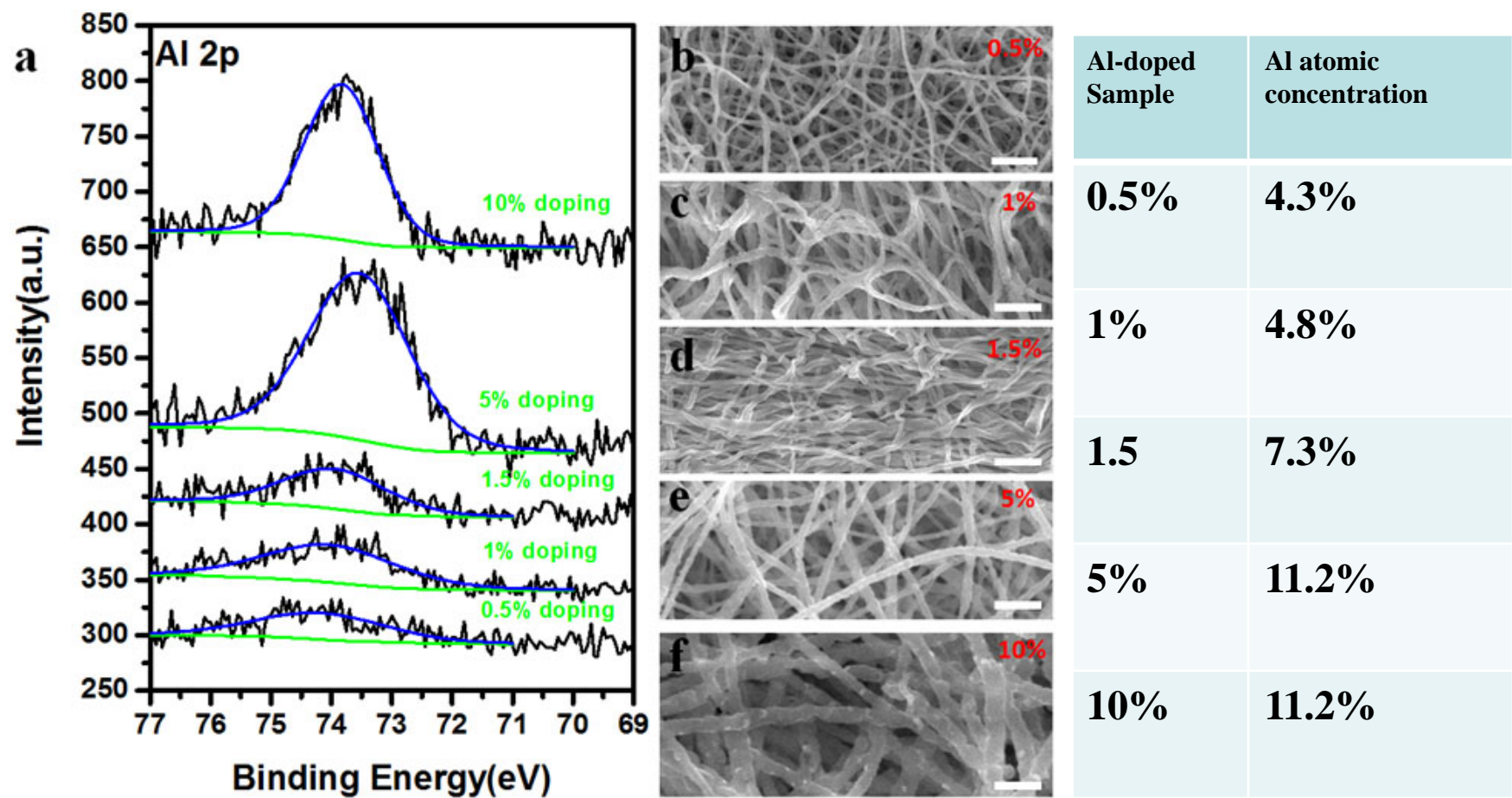
Morphologies and structure of 0.5 mol% Al doped LLATO nanofibers



- After calcinations at 900 $^\circ\text{C}$ in air, all of the diffraction peaks from 0.5-10 mol % Al doped LLTO proved single-phase perovskite $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$.
- Ionic conductivity of Al-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLATO) is **$1.1 \times 10^{-3} \text{ S/cm}$** .

Inorganic Nanofibers: *Al-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLATO)*

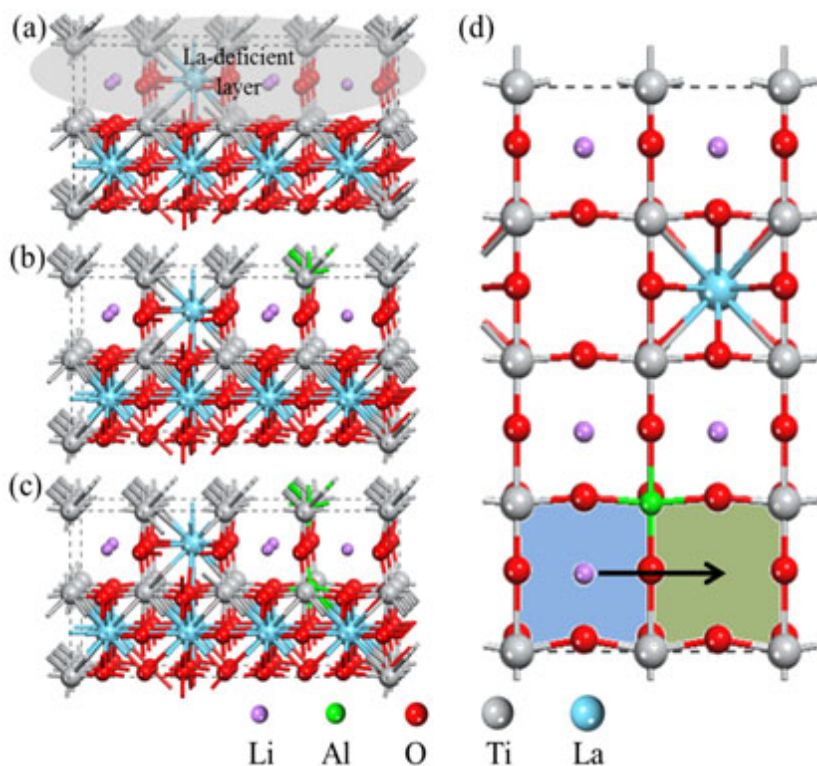
XPS spectra of LLATO with different Al contents:



XPS spectra of Al 2p for LLATO with different Al contents (0.5%, 1%, 1.5%, 5%, 10% doping). The spectra show a peak around 73.5 eV, which shifts to higher binding energy as the Al content increases. SEM images (b-f) show the morphology of the nanofibers for each Al content, with scale bars indicating the size.

Inorganic Nanofibers: *Al-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLATO)*

Theory calculation of Al-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ structure:



Constructing La-full and La-deficient layers along stuck direction in the left figure, we studied the transporting behavior of Li ions in pure and Al-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$. The left figure gives ideal transporting direction to simplify our research.

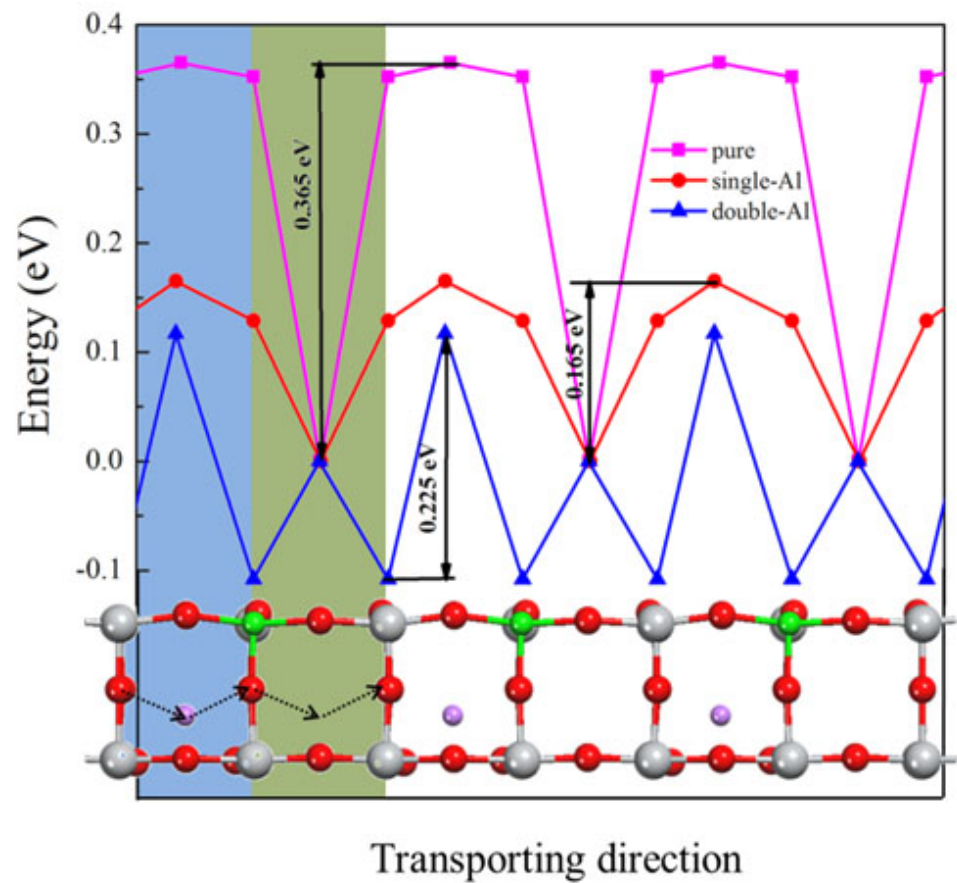
Pure and Al-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$.

(a), (b) and (c) are side views of pure, most stable single-Al and double-Al doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$, respectively.

(d) is the top view of La-deficient layer of (b). Blue and green color blocks in (d) are used to represent two different regions in Li atom transporting direction.

Inorganic Nanofibers: *Al-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLATO)*

Theory calculation of Al-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ structure:



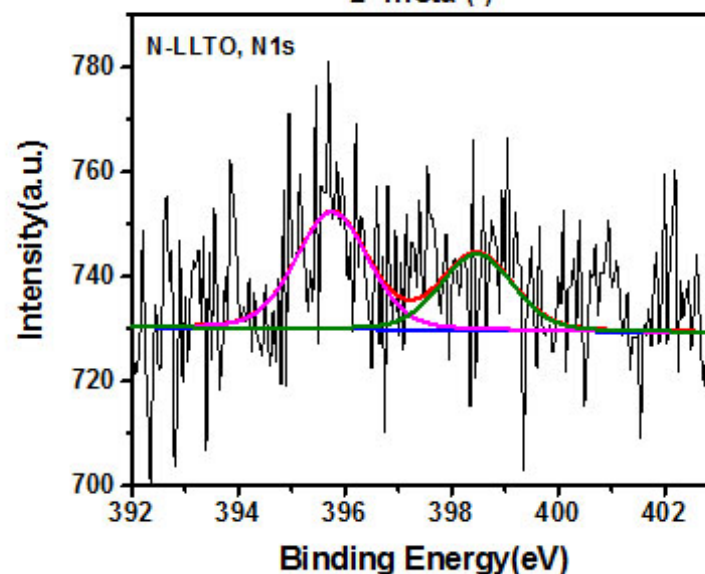
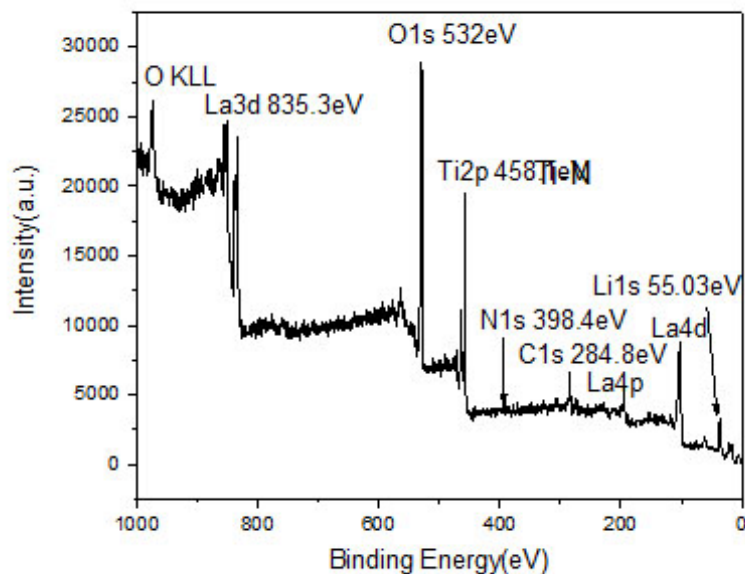
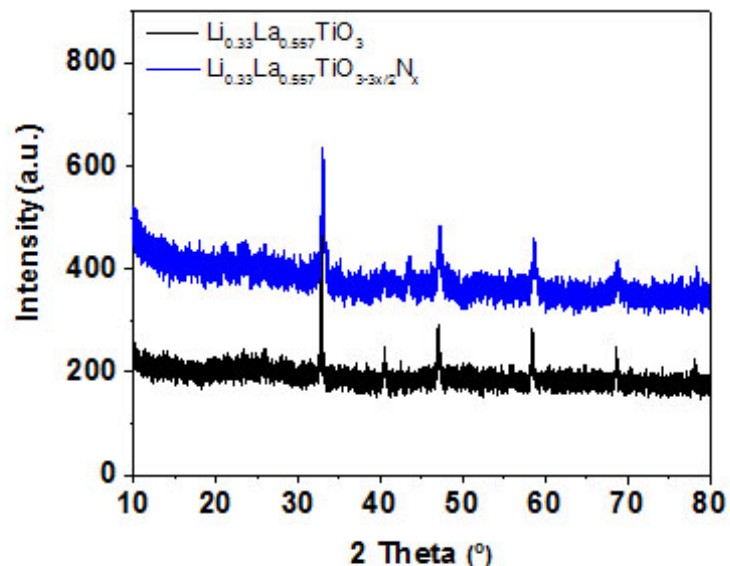
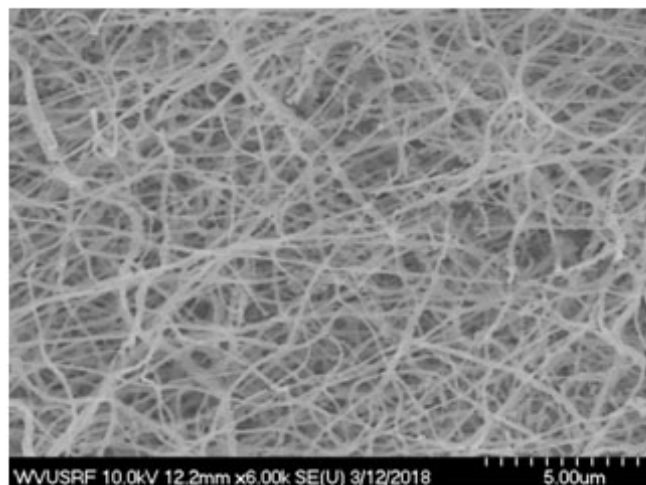
Transporting barriers for Li ions along transporting direction in pure, single-Al and double-Al doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$. The transporting trajectory is marked by dash line in inset.

Transporting barrier for pure, single-Al and double-Al doped structure are 0.365 eV, 0.165 eV and 0.225 eV, respectively. This trend is consistent with experiments.

Al content (mol%)	0	0.5	1	1.5	5	10
Ionic conductivity (10^{-4} S/cm)	1.10	3.98	3.62	1.96	1.08	0.81

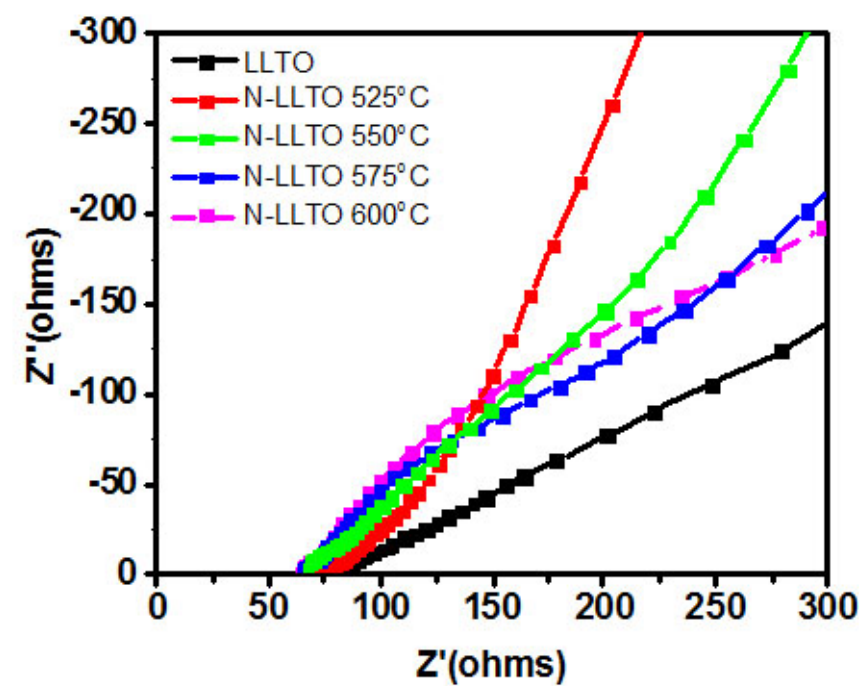
Inorganic Nanofibers: *Nitrogen-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (N-LLTO)*

Morphologies, XRD patterns and XPS spectrum of N-doped LLTO nanofibers:

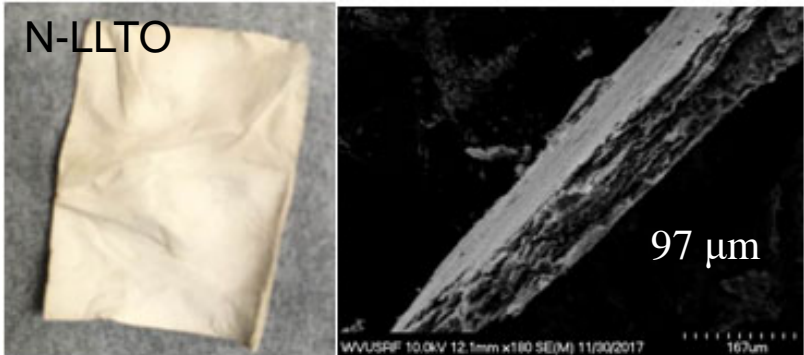


Inorganic Nanofibers: *Nitrogen-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (N-LLTO)*

EIS plots of N-LLTO under different doping temperature:



LLTO /PVDF-HFP	Pure LLTO	N-525°C	N-550°C	N-575°C	N-600°C
Ionic conductivity ($\times 10^{-4}$ S/cm)	1.3	2.1	3.8	2.3	2.3

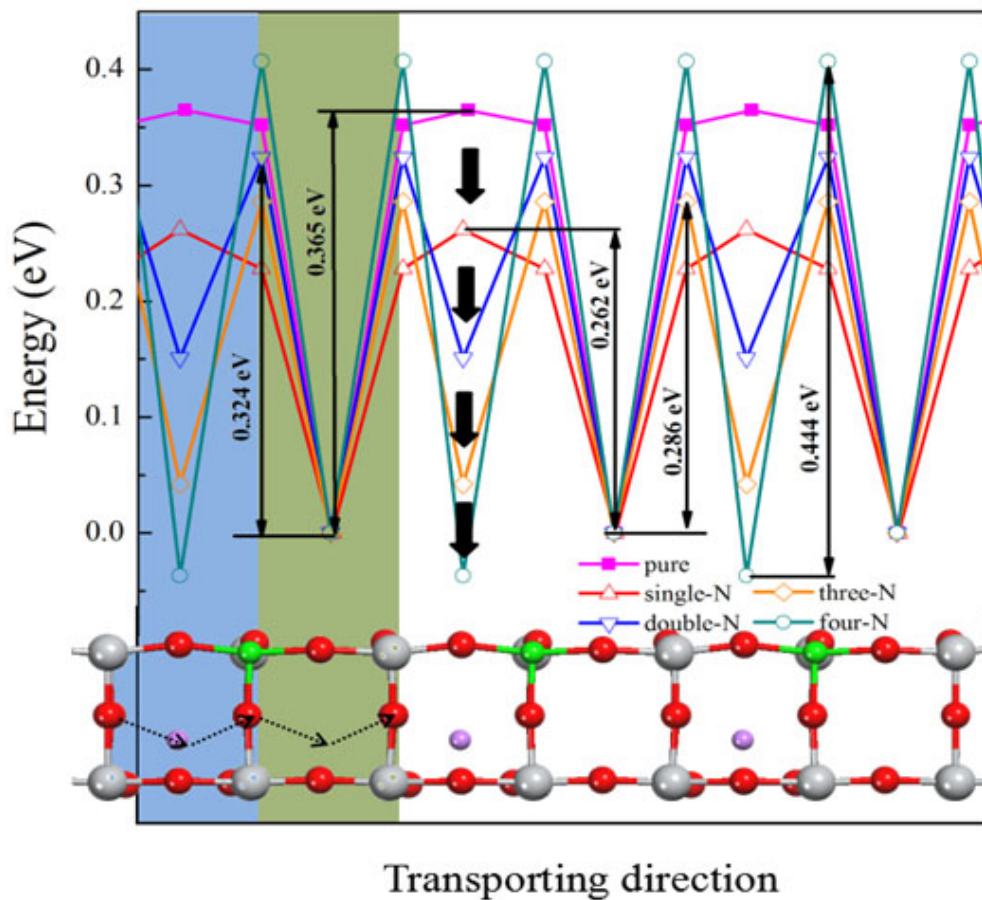


N content in N-LLTO

Temperature °C	525	550	575	600
N content	-	0.8%	0.9%	1.0%

Inorganic Nanofibers: *Nitrogen-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (N-LLTO)*

Theory calculation of N-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ structure:



Hypothesis: Nitrogen doping may:

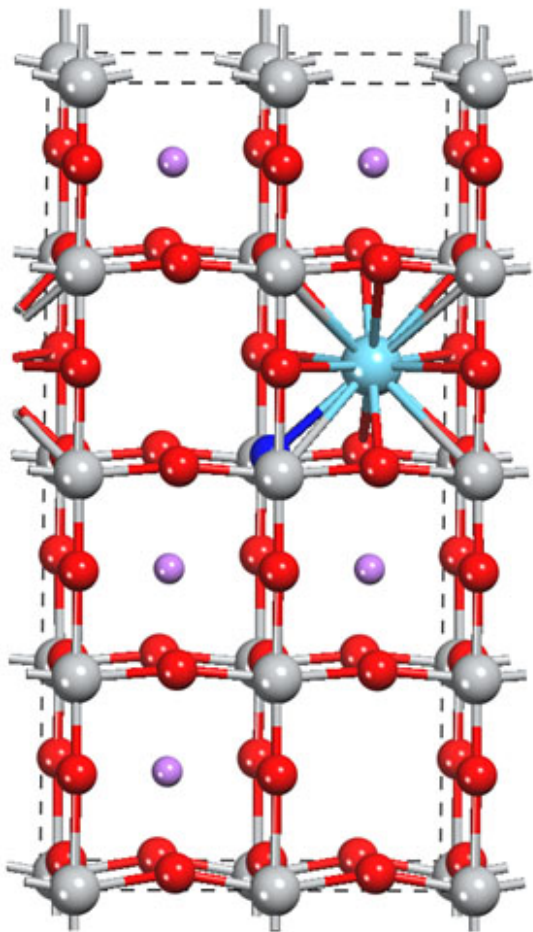
- Decrease the transporting barrier.
- Generate of oxygen vacancies, e.g. $\text{ABO}_3 / \text{ABO}_{3-3x/2}\text{N}_x$

Doping nitrogen to $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ can reduce the transport barrier for Li ions. However, over-doping of N atoms could hamper Li atom transport. Single-N dopant in $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ results in the lowest transport barrier of 0.262 eV. This is consistent with experiments.

Relative energy for pure and N-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ in transport direction of Li ions. Blue balls indicate N atoms.

Inorganic Nanofibers: *Nitrogen-doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (N-LLTO)*

Theory calculation of N-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$:



Hypothesis: Nitrogen doping may:

- Decrease the Li-ion transport barrier.
- Generate of oxygen vacancies, e.g. $\text{ABO}_3/\text{ABO}_{3-3x/2}\text{N}_x$

$$E_{\text{formation}} = E_{\text{single N-dopant}} + E_{\text{O-vacancy}} - 1/2E_{\text{O}_2}$$

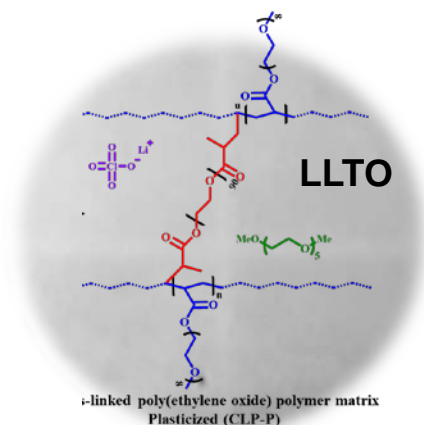
- Formation energy for O-vacancy is -3.167 eV, which indicates that O-vacancy formation was in favor thermodynamically
- Li-ion transport barrier is 0.277 eV, lower than pure LLTO (0.365 eV).

Most stable O-vacancy in single N-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$

Current Progress in

***CERAMIC-POLYMER COMPOSITE
ELECTROLYTE***

Composite electrolytes developed

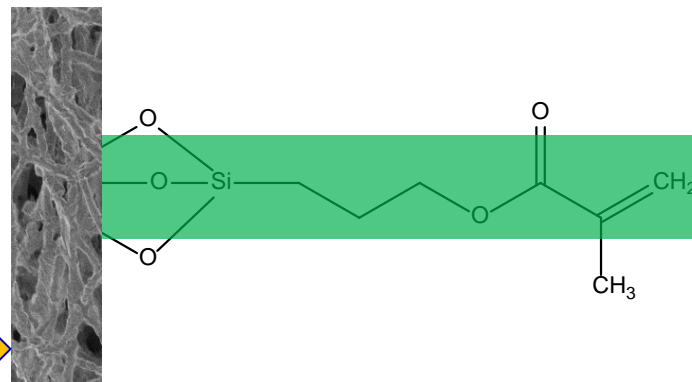


Composite electrolyte 1:

LLTO incorporated cross-linked polymer

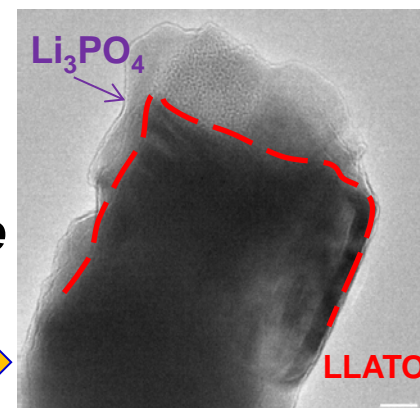
Composite electrolyte 2:

Silane-LLAZO incorporated cross-linked polymer composite electrolyte

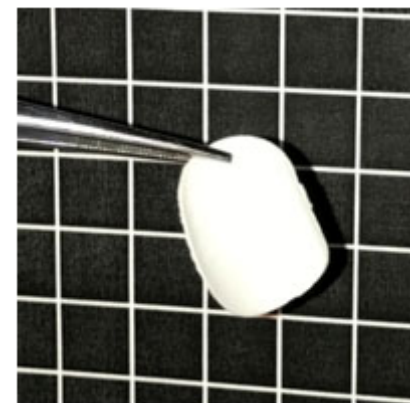
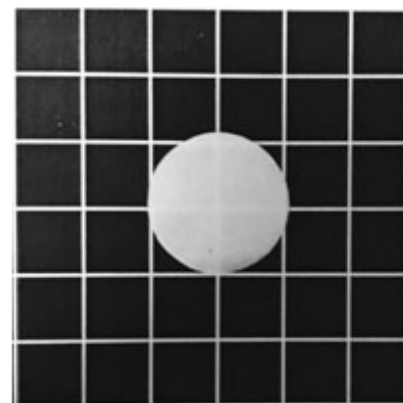
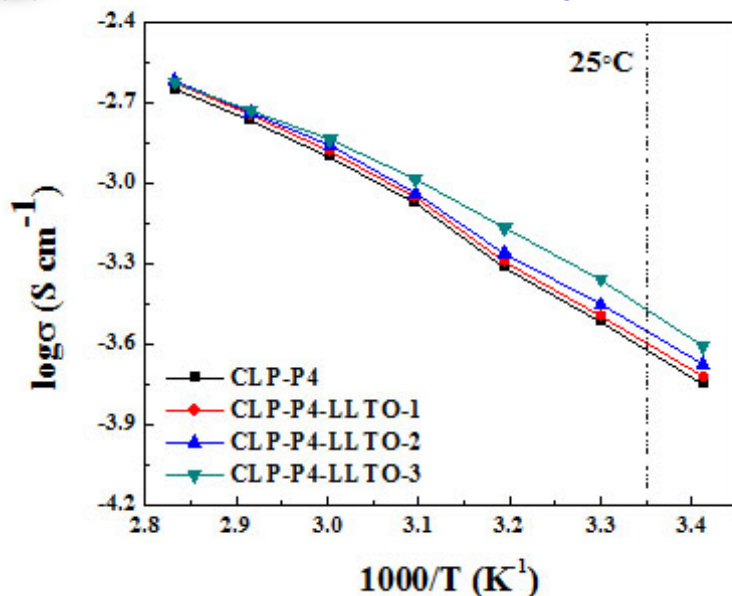


Composite electrolyte 3:

Lithium phosphate modified LLATO based composite electrolyte



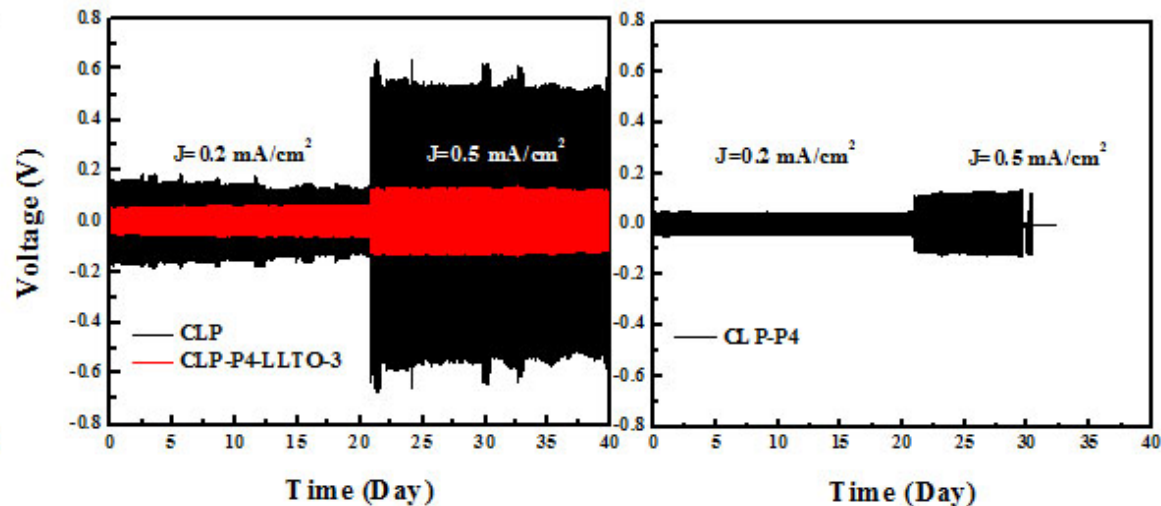
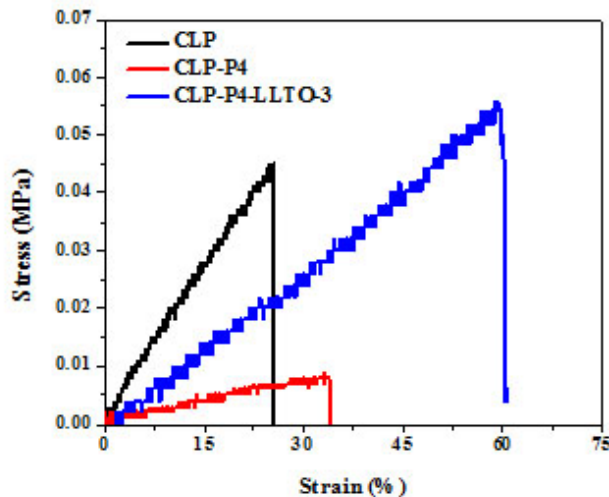
Ionic conductivity



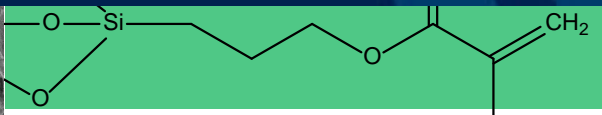
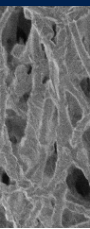
- Adding inorganic nanofibers leads to an increase in ionic conductivity
- No agglomeration effect was observed (lithium transference number (t) increases with the addition of LLTO nanofibers)
 - Well-distribution of nanofibers
 - Naturally amorphous polymer matrix
- Significantly enhance lithium transference number

	LLTO amount (wt %)	Ionic conductivity at 25 °C (S cm ⁻¹)	t_{Li^+}
CLP	0	3.38×10^{-5}	0.15
CLP-P4	0	2.40×10^{-4}	0.15
CLP-P4-LLTO-1	10	2.48×10^{-4}	0.26
CLP-P4-LLTO-2	20	2.82×10^{-4}	0.40
CLP-P4-LLTO-3	30	3.31×10^{-4}	0.51

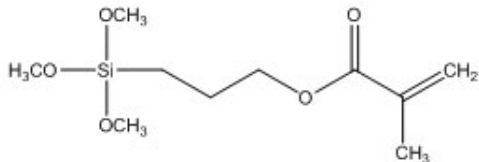
Mechanical property and cycling stability:



- Young's Modulus
 - CLP: 0.21 MPa
 - CLP-P4: 0.02 MPa
 - CLP-P4-LLTO-3: 0.13 MPa
- Tensile strength
 - CLP: 0.18 MPa
 - CLP-P4: 0.02 MPa
 - CLP-P4-LLTO-3: 0.10 MPa
- Symmetric lithium cells: Li|SEs|Li
 - Charge/discharge at constant current densities
 - 0.2, 0.5 mA/cm² for 15 min at room temperature
- CLP-P4 symmetric cell short-circuits after 30 day
 - Short-circuit because of the mechanical failure
 - without the presence of LLTO nanofibers
- LLTO nanofibers provided a mechanically robust framework, and the resultant CLP-P4-LLTO-3 cell shows stable charge/discharge process after 30 days

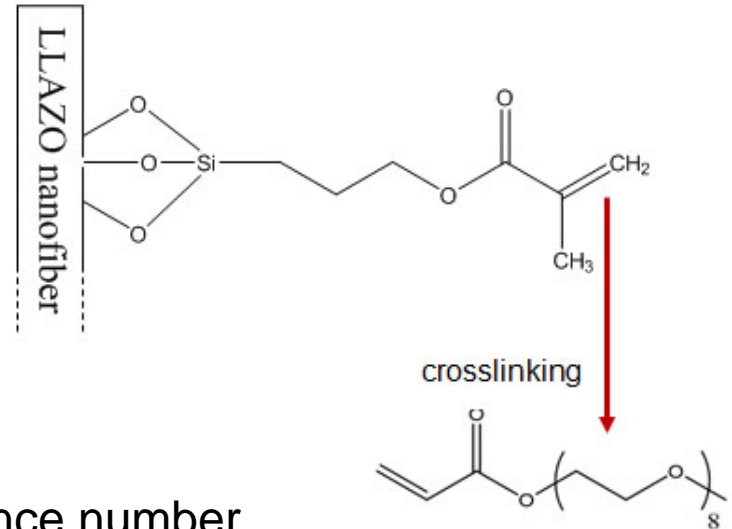


Silane



$\text{Li}_{6.4}\text{La}_3\text{Al}_{0.24}\text{Zr}_2\text{O}_{12}$ (LLAZO)

Ethanol/ H_2O (95:5)
Acetic Acid (PH~4.5)

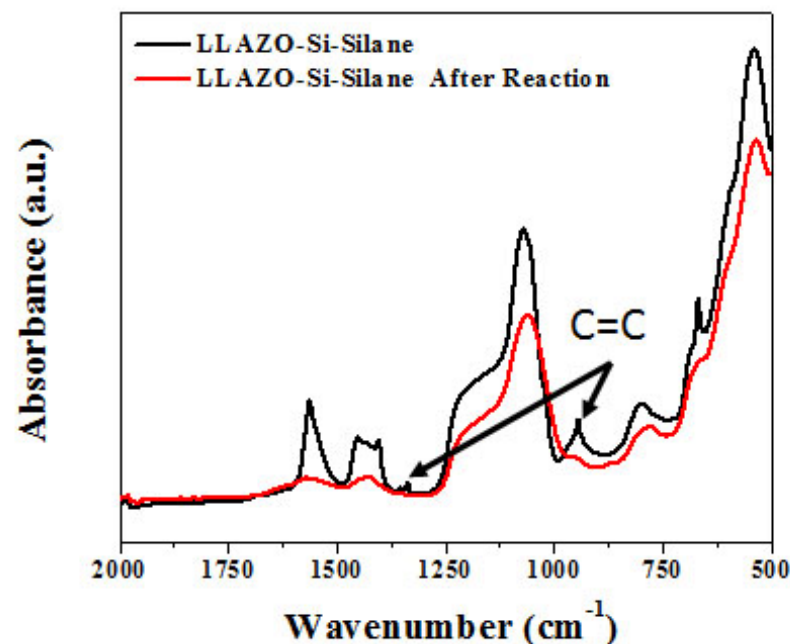
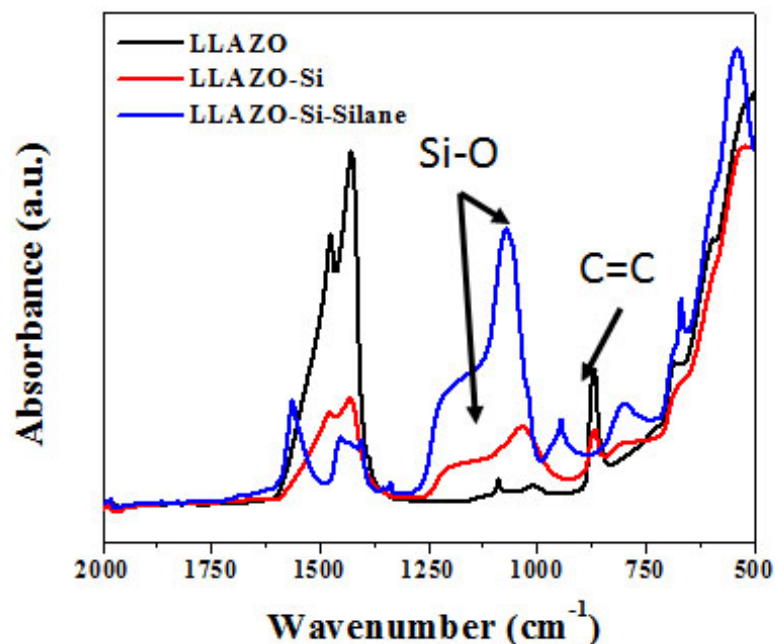


- Reduce the interfacial resistance
- High ionic conductivity, high lithium transference number

Synthesis process (Preliminary approach)

- SiO_2 coating
 - 3 wt% tetraethyl orthosilicate (TEOS) in ethanol/ H_2O (95:5 volume ratio) for 30 min
- Silane coating
 - 2.5 wt% 3-(Trimethoxysilyl)propyl methacrylate (Silane) in ethanol/ H_2O (95:5 volume ratio) for 12 h

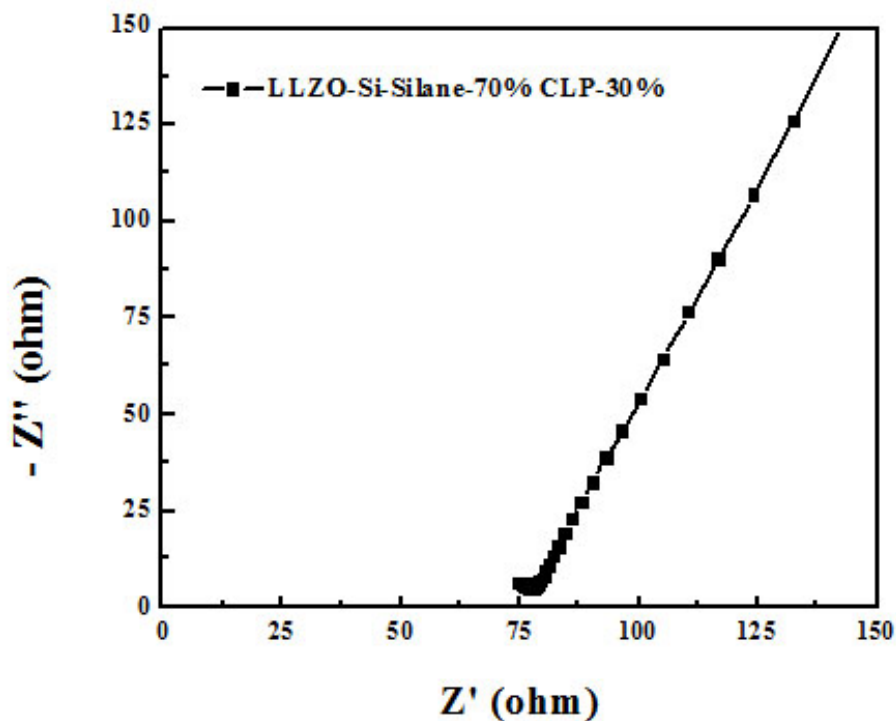
Chemical characterization:



- SiO_2 and silane are successfully coated on the surface of LLAZO nanofibers
 - Si-O groups, C=C groups appear
- The vinyl groups of silane coating layer is active and can be cross-linked by thermal initiators
 - C=C groups disappear after polymerization

Composite electrolyte 2:

Electrochemical testing:



- Ionic conductivity test methods
 - Solution casting membrane without pressing into pellets
- Thicker coating layer reduces the overall impedance

Preliminary results:

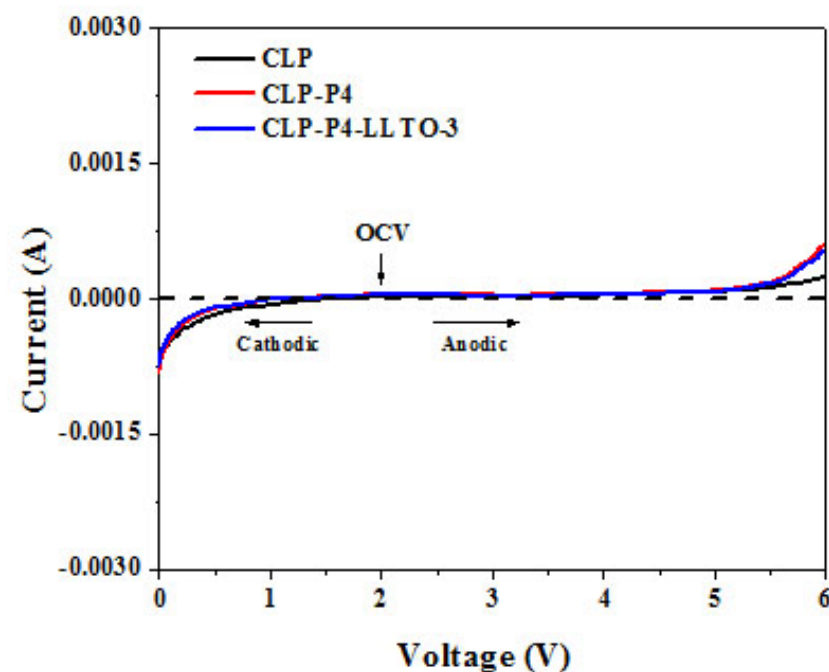
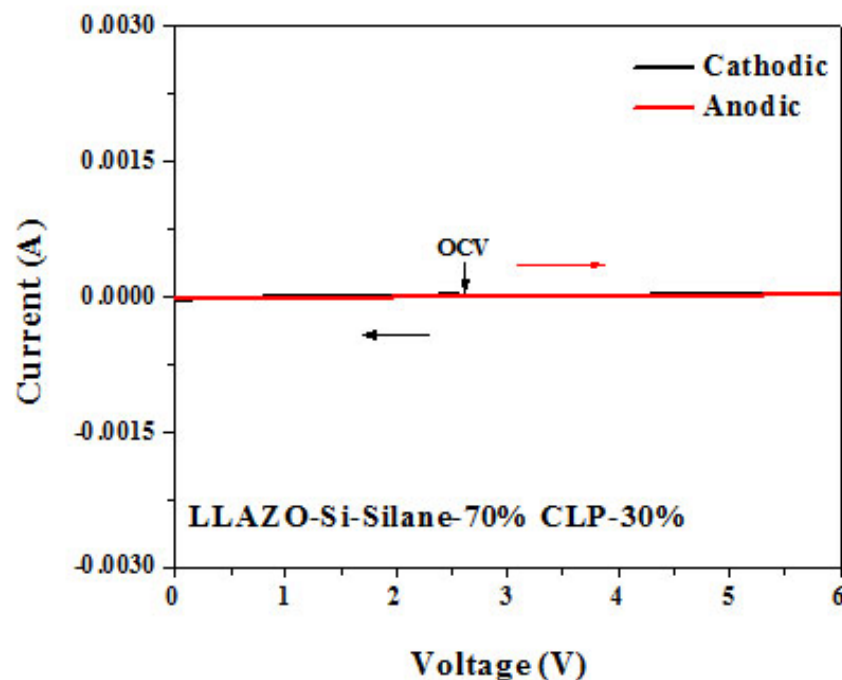
- 70 wt% LLAZO-silane + 30 wt% CLP
 - Ionic conductivity $3.78 \times 10^{-4} \text{ S/cm}$ at room temperature

- Vary the silane coating thickness
 - 3h, 6h, 12h and 24h
- Vary the composition of silane coated LLAZO and CLP monomers
 - 70 wt% LLAZO-silane + 30 wt% CLP
 - 80 wt% LLAZO-silane + 20 wt% CLP
 - 90 wt% LLAZO-silane + 10 wt% CLP

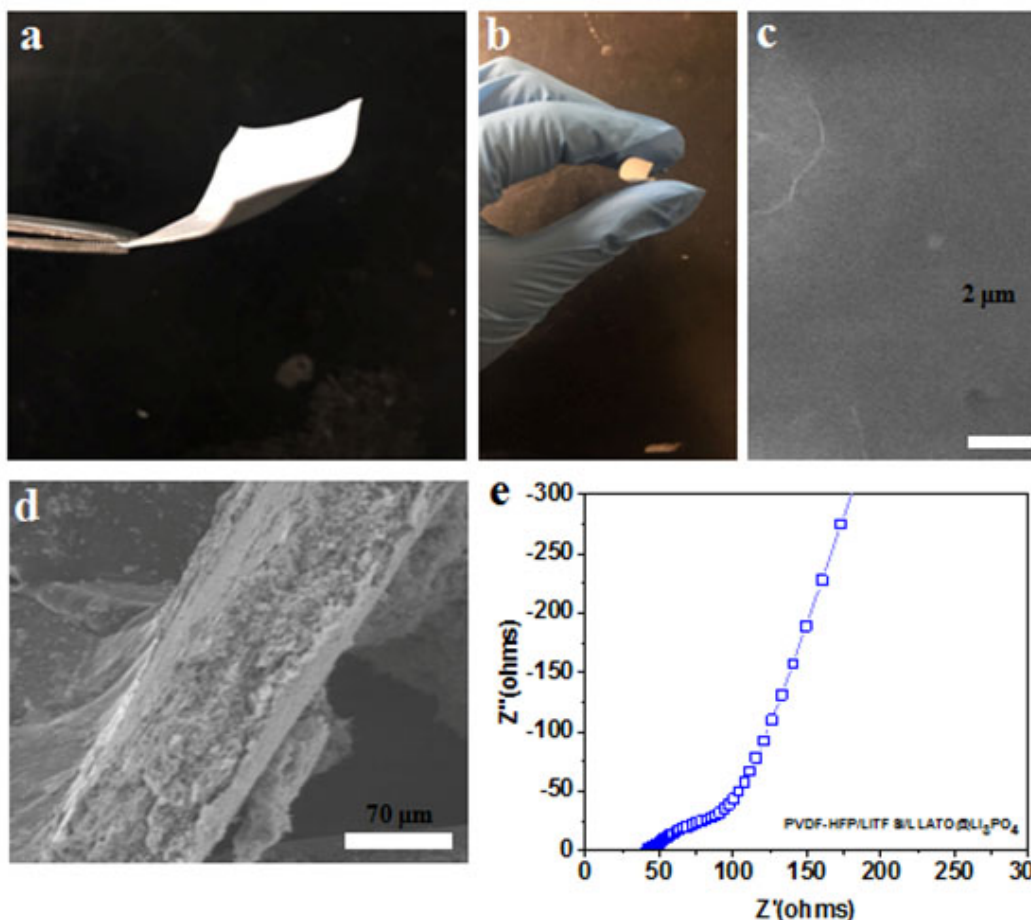
Composite electrolyte 2:

Silane-LLAZO incorporated cross-linked polymer composite electrolyte

Electrochemical testing:



- Much more stable than CLP polymer electrolyte and CLP composite electrolyte
 - 0 ~ 6 V for LLAZO-Si-Silane-70% CLP-30% composite electrolyte
 - 1 ~ 5 V for CLP, CLP-P4, and CLP-P4-LLTO-3



The coating of the Li_3PO_4 layer improves the ionic conductivity to $5.09 \times 10^{-4} \text{ S/cm}$ by 26.9% compared with PVDF-HFP/LiTFSI/LLATO.

(a), (b) Photograph of flexible and bendable PVDF-HFP/LiTFSI/LLATO membrane

(c) SEM image of the surface of PVDF-HFP/LiTFSI/LLATO membrane,

(d) cross-sectional SEM image of PVDF-HFP/LiTFSI/LLATO membrane,

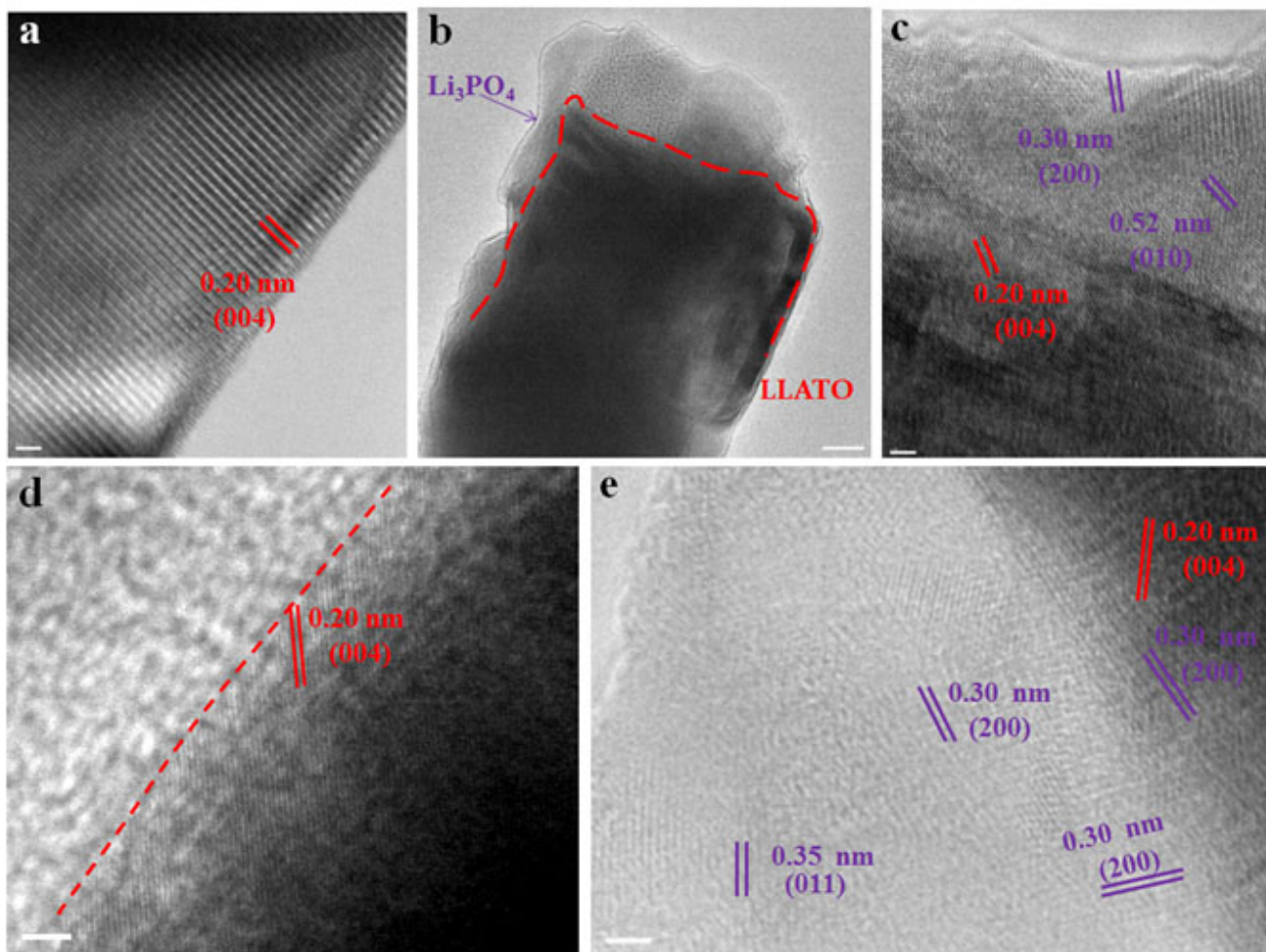
(e) EIS profiles of the PVDF-HFP/LiTFSI/LLATO(black),PVDF-HFP/LiTFSI/LLATO(red),PVDF-HFP/LiTFSI/LLATO- Li_3PO_4 (blue) electrolyte membrane at different temperatures(inert is the zoom plots).

Al doping percent(mol%)	0	0.5	1	1.5	5	10	0.5/ Li_3PO_4
Ionic conductivity (10^{-4} S/cm)	1.10	3.98	3.62	1.96	1.08	0.81	5.09

Composite electrolyte 3:

Lithium phosphate modified LLATO-polymer composite electrolyte

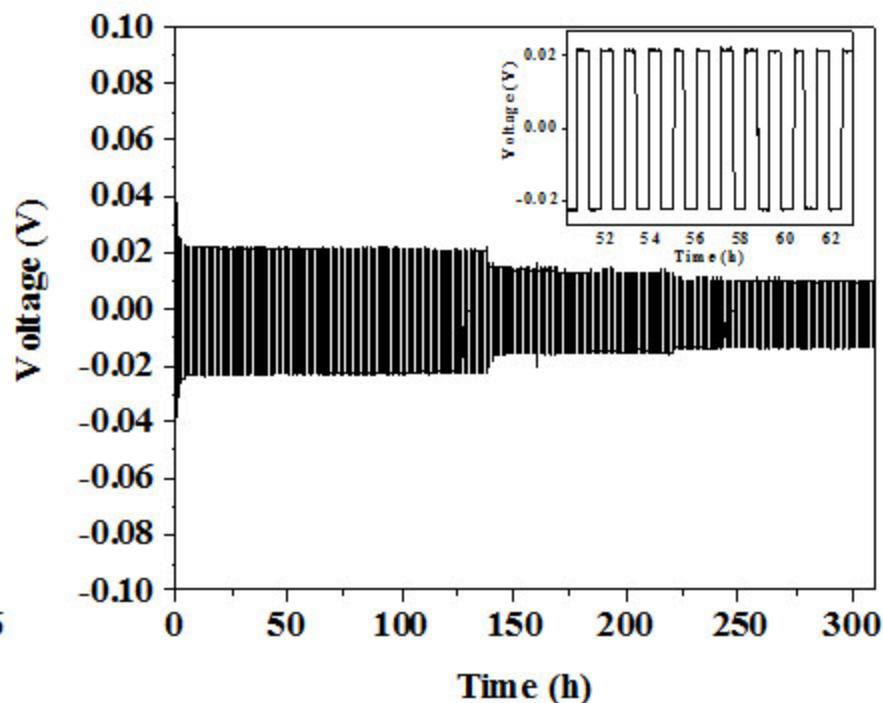
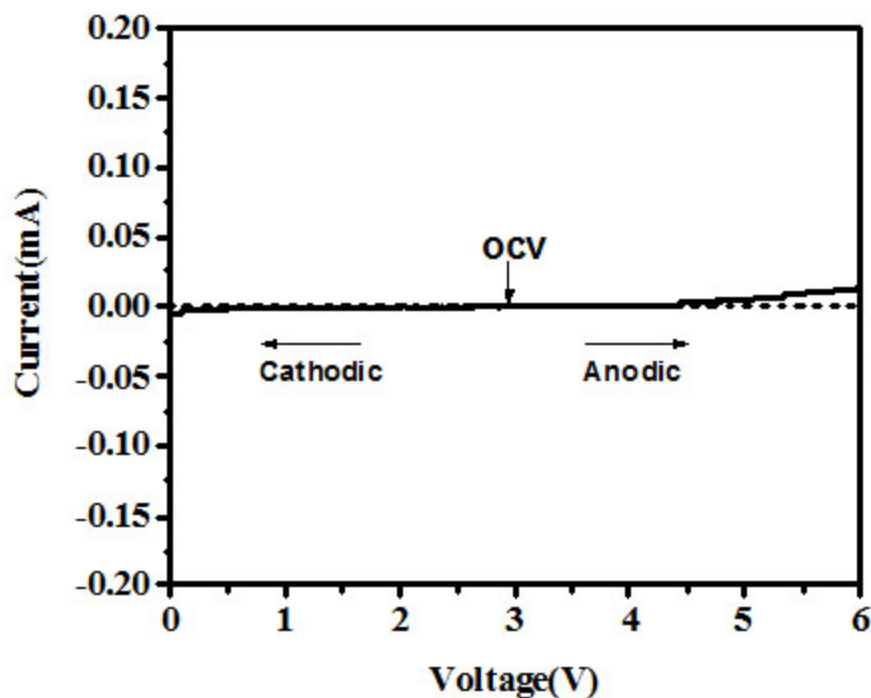
Microstructure characterization:



(a) TEM image of LLATO nanofibers, (b) TEM (c) HRTEM image of Li₃PO₄ modified 0.5% Al-LLATO nanofibers, (d) interface of PVDF-HFP/LiTFSI/LLATO composite (e) interface of PVDF-HFP/LiTFSI/LLATO/Li₃PO₄ composite .

Composite electrolyte 3:

Electrochemical testing:



- Electrochemical window
 - 0~6 V for of PVDF-HFP/LiTFSI/LLATO/Li₃PO₄ composite electrolyte
- Symmetric lithium cells: Li|SEs|Li
 - Charge/discharge at constant current densities
 - Small polarization voltages of ± 23 mV were observed at 0.5 mA/cm² for 30 min at room temperature

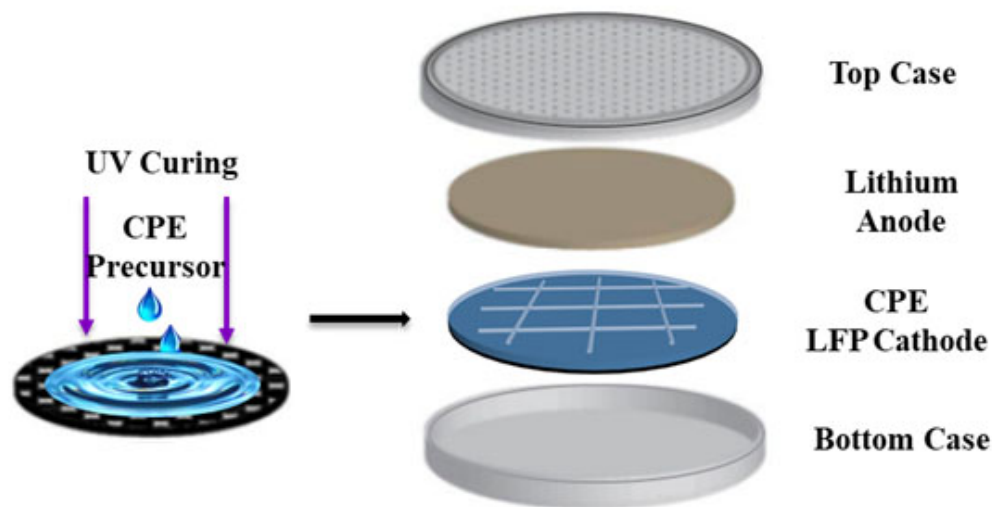
Current Progress in

COIN-CELL BATTERY

Battery performance: *Fabrication of coin cells*

Battery assembly:

- **Cathode:** LiFePO_4 (LFP)
 - Cathode composition
LFP: CLP-P4-LLTO : C = 6 : 3 : 1
LFP loading: 2 mg/cm^2
- **Anode:** Lithium foil
- **Electrolyte:** LLTO incorporated cross-linked polymer composite electrolyte CLP-P4-LLTO

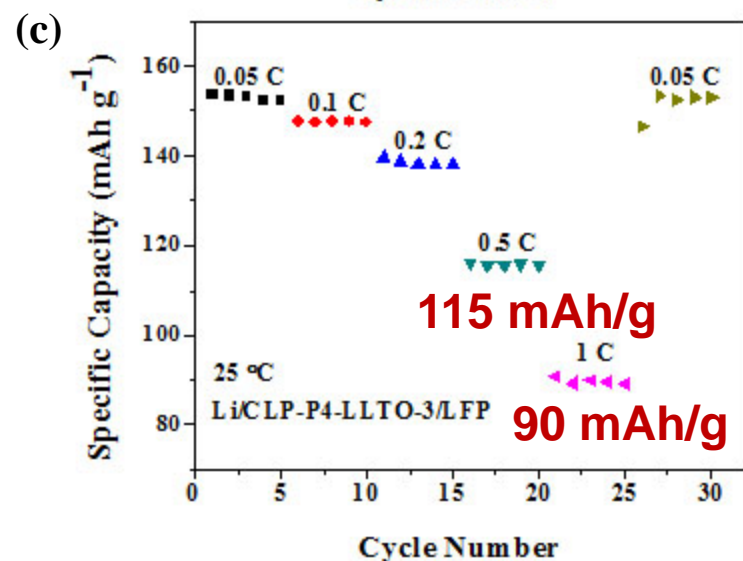
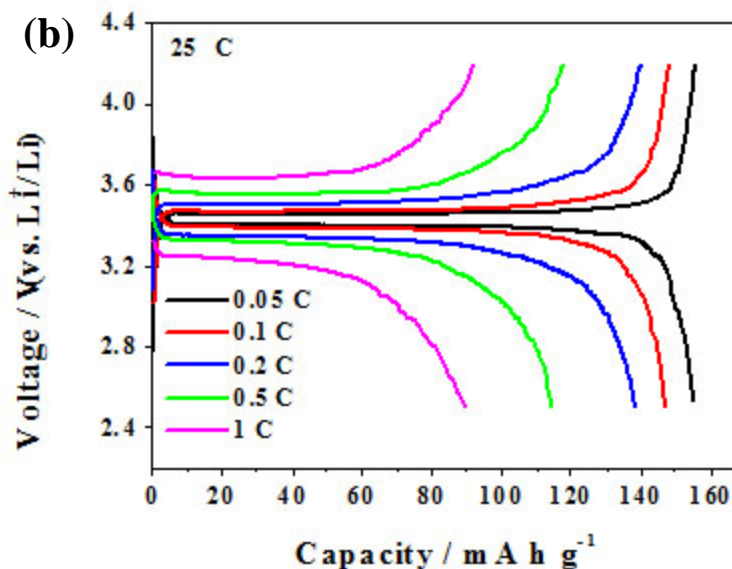
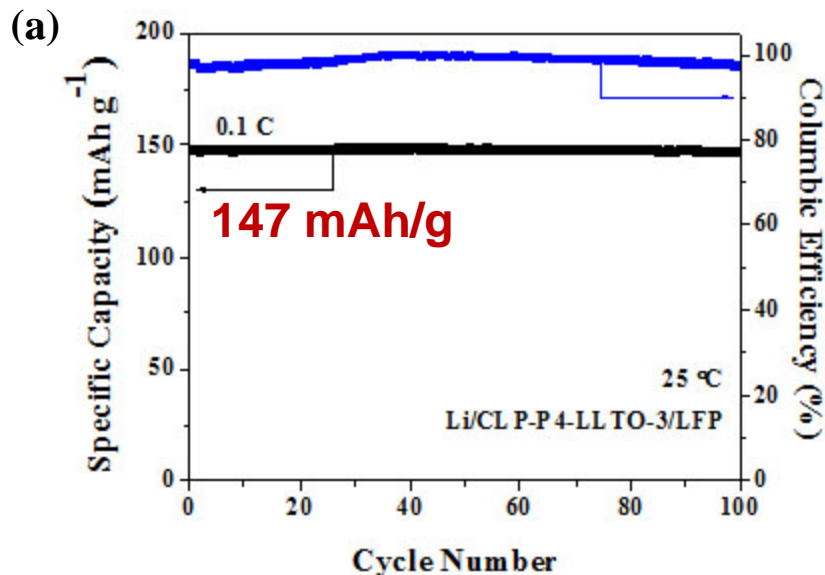


To improve contact between electrolyte and cathode:

- Precursor
- Polymerization under UV light directly on cathode
- Heat at 80°C for 20 mins after assembling

Battery performance

Electrochemical testing:



- Perfect harmony of plasticizer and nanofibers
 - High Li^+ conductivity
 - Good mechanical properties
- Excellent cycle-stability-
 - High capacity retention of ~98%
 - High columbic efficiency of 99%
- Excellent rate capability
 - 115 mAh/g at 0.5 C,
 - 90 mAh/g at 1 C

Collaboration and Coordination with Other Institutions



U.S. Department of Energy
-Sponsorship, steering



West Virginia University - Project lead
Management and coordination; inorganic nanofiber design, synthesis and characterization; composite electrolyte development; and battery construction and testing



North Carolina State University - Key partner
Polymer matrix design, synthesis and characterization; linker development; and full cell construction and testing



Quzhou University
Theory calculations on the cationic and anionic doping of perovskite materials

Remaining Challenges and Barriers

- It remains a significant challenge in improving the ionic conductivity of polymer matrix in the composite.
- It is essential to explore the synergistic effect of polymer and ceramic nanofibers.
- A grafting agent with high ionic conductivity is expected to promote the Li ion transport between the ceramic nanofibers and the polymer matrix. However, such an organic linker is rare.
- The solid-state interface between the electrolyte and the electrode has significant effect on the performance of full-cell batteries. The fabrication processes need to be explored to optimize the interface.

Proposed Future Research

Polymer matrix:

- Optimize and develop new polymer structures with high ionic conductivity

Inorganic ceramic nanofibers:

- Improve the ionic conductivity of nanofibers by doping
- Coating the ceramic nanofiber surface by a high ionic conductivity layer

Composite electrolytes:

- Search for a grating agent with high ionic conductivity
- Modify the ceramic nanofiber surface to create a buffer layer at the ceramic-polymer interface

Batteries:

- Construct and test Li/composite electrolyte/Li symmetric cells
- Construct and test Li/composite electrolyte/cathode full cells
- Optimize the composition and structure of the full cells

Summary

For polymer matrix, reached the goal of 2×10^{-4} S/cm :

- Three major polymer matrices have been successfully synthesized
- The PEO cross-linked polymer exhibits high ionic conductivity of 2.40×10^{-4} S/cm at room temperature

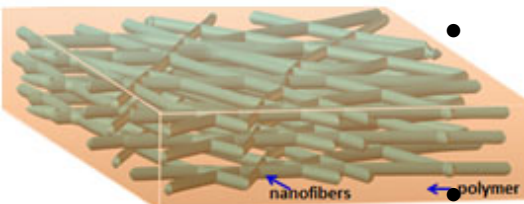
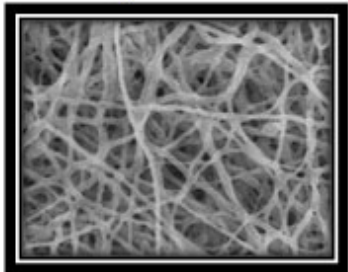
For inorganic nanofibers, reached the goal of 1×10^{-3} S/cm :

- 0.5% aluminum doped $\text{Li}_{0.33}\text{La}_{0.56}\text{Ti}_{0.995}\text{Al}_{0.005}\text{O}_3$ (LLATO) nanofibers exhibits ionic conductivity of 1.08×10^{-3} S/cm.

For Composite electrolyte:

- The LLTO nanofiber/CLP-P4 composite electrolyte exhibits improved mechanical properties and enhanced lithium transference number as compare to the polymer alone.
- New type of composite electrolyte was prepared with silane-coated LLAZO nanofibers and CLP. The composite electrolyte exhibits ionic conductivity of 3.78×10^{-4} S/cm and stable electrochemical window.

The composite electrolyte consisting of Li_3PO_4 -modified LLATO nanofibers and PVDF-HFP exhibits ionic conductivity of 5.1×10^{-4} S/cm, as well as stable and wide electrochemical window.



Responses to Previous Year Reviewers' Comments

No previous comments